Renewable and Sustainable Energy Reviews 29 (2014) 546–564

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Review on latest developments in biodiesel production using carbon-based catalysts

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ARTICLE INFO

Article history:
Received 6 August 2012
Received in revised form
23 May 2013
Accepted 2 September 2013
Available online 24 September 2013

Keywords:
Activated carbon
Catalyst support
Carbon catalysts
Sulfonation
Transesterification
Biodiesel

ABSTRACT

Catalyst plays an important role in biodiesel production. Owing to the advantages of heterogeneous catalysts in terms of separation and reusability over the traditionally used homogeneous catalyst, the research has now been focused on these heterogeneous catalysts in recent years. In order to make the process fully "green", researchers are trying to prepare catalysts from renewable sources such as biomass. Within this concept the carbon based catalysts have been introduced. Carbon based materials are considered as ideal catalysts due to desirable features such as low material cost, high surface area and thermal stability. They are easily prepared by functionalizing carbon surface with acids or bases; in other cases carbon material was reported to be used as a support. Additionally, the carbon could be produced from most of the waste generated in different industrial processes. Therefore, its utilization as catalyst makes the biodiesel production a "greener" one. Under optimal conditions biodiesel (FAME) yields up to 90–98.3% were reported over various carbon based catalysts.

Contents

1. Introduction

Due to the continuous decline of limited petroleum reserves and the growing environmental concerns, the use of biodiesel in recent years as a fuel in the existing diesel engines has gained much importance [1]. Current generation biodiesel production usually utilizes homogeneous transesterification of vegetable oils with strong alkali (NaOH, KOH) as catalysts [2]. The process has many limitations, a considerable amount of energy is required for the purification of products and catalyst separation, and furthermore these catalysts are not reusable. This results in substantial energy wastage and the production of large amounts of chemical waste. Strong acids such as H_2SO_4, HCl can also catalyze this reaction but at a much slower rate limiting their industrial applicability [3]. Enzymes such as lipase can also do the same but the process is not economically viable [4]. In order to overcome these issues researchers have utilized different heterogeneous catalysts (both acidic and basic) for transesterification.

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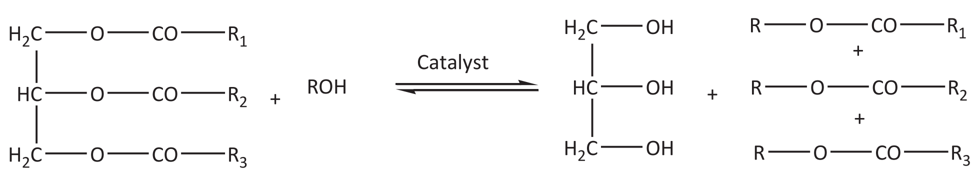
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http://dx.doi.org/10.1016/j.rser.2013.09.003

These catalysts can be readily separated from the products at the end of the reaction and reused for the next reaction cycle [5,6]. This has been demonstrated by different catalysts reported such as supported alkali metal catalysts [7], alkali and alkaline earth oxides, mixed metal oxides [5,8], dolomites perovskite-type catalysts and zeolites [9], heteropolyacids [10], Amberlyst-15 [11], $H_3PW_{12}O_{40}\cdot 6H_2O$ [12], WO_3/ZrO_2 [13], hydrotalcite and so on [14]. Ionic liquids have also been explored as catalysts in transesterification [15]. However, most of the ionic liquid catalysts reported so far utilized complex and expensive synthesis routes, demonstrated poor reusability and were non-biodegradable. Moreover, none of the catalysts were capable of showing activity comparable to alkali metal hydroxides. To address these issues, catalyst research for the production of cost effective biodiesel has been focused towards low cost renewable "green catalyst". Such a novel catalyst could be prepared either from biomass or from waste generated from it in the households. Recently renewable heterogeneous catalysts such as metal oxides catalysts derived from oyster shells [16], shrimp shell [17,18], eggshells [19,20] and carbon-based catalysts [21–23] have gained much importance owing to their low material costs which could significantly bring down the biodiesel production cost. Many review papers regarding biodiesel feedstocks, properties, characterization and the development of heterogeneous catalysts in biodiesel production have been published in recent years. In some of the review papers the reviewers have divided the heterogeneous catalysts into different categories such as oxides, mixed metal oxides, and zeolites. However, review on the carbon based catalyst has rarely been mentioned in most of the review papers. The focus of this review paper is to present the latest research on carbon based catalysts, specific outcome and its importance in environmentally benign biodiesel production.

1.1. Overview of biodiesel production by transesterification

Conventional biodiesel production is based on the transesterification of triglycerides and alcohols (Scheme 1). Transesterification is the general term used to describe the important class of organic reactions where one ester is transformed into another ester through interchange of the alkoxy moiety.

Transesterification is the easiest and the most cost effective way to produce biodiesel. The reaction can be catalyzed by an acid or a base, in principle transesterification proceeds most efficiently on base catalysts. The overall economy of biodiesel production depends mainly on two crucial factors: (i) feedstock and (ii) catalyst (determines the no of steps and synthesis route). Nearly all the biodiesel plants are currently using refined vegetable oils such as soybean, rapeseed, and cottonseed as main feedstock and contribute nearly 80% of the overall biodiesel production cost [24]. In order to overcome these limitations and ensure economic



Scheme 1. Biodiesel production by transesterification.

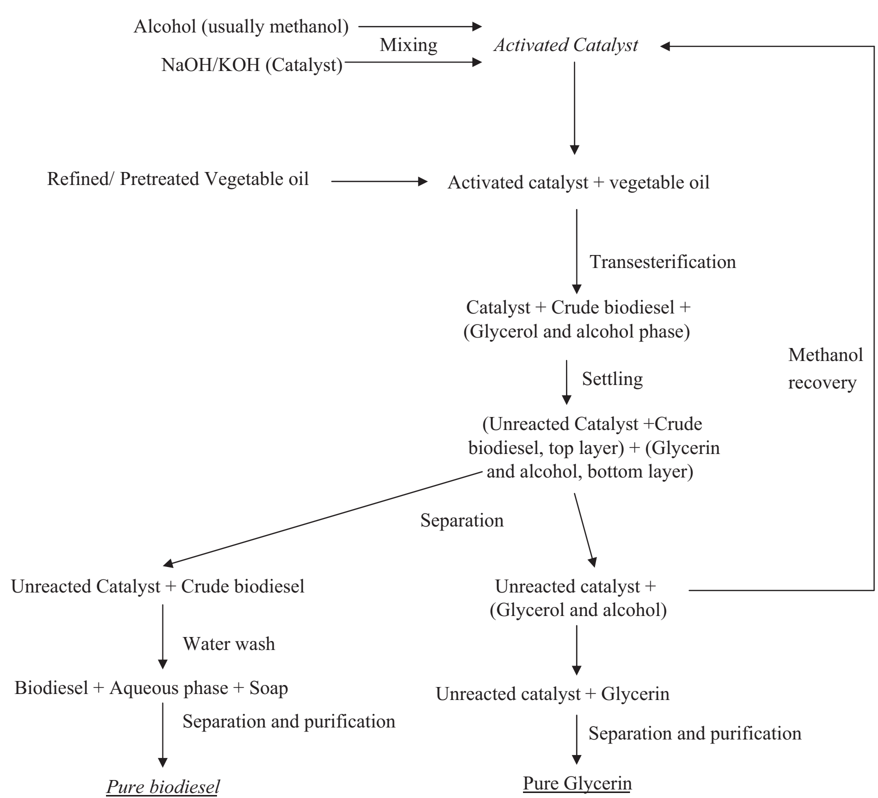


Fig. 1. Schematic block diagram of homogeneous biodiesel production.

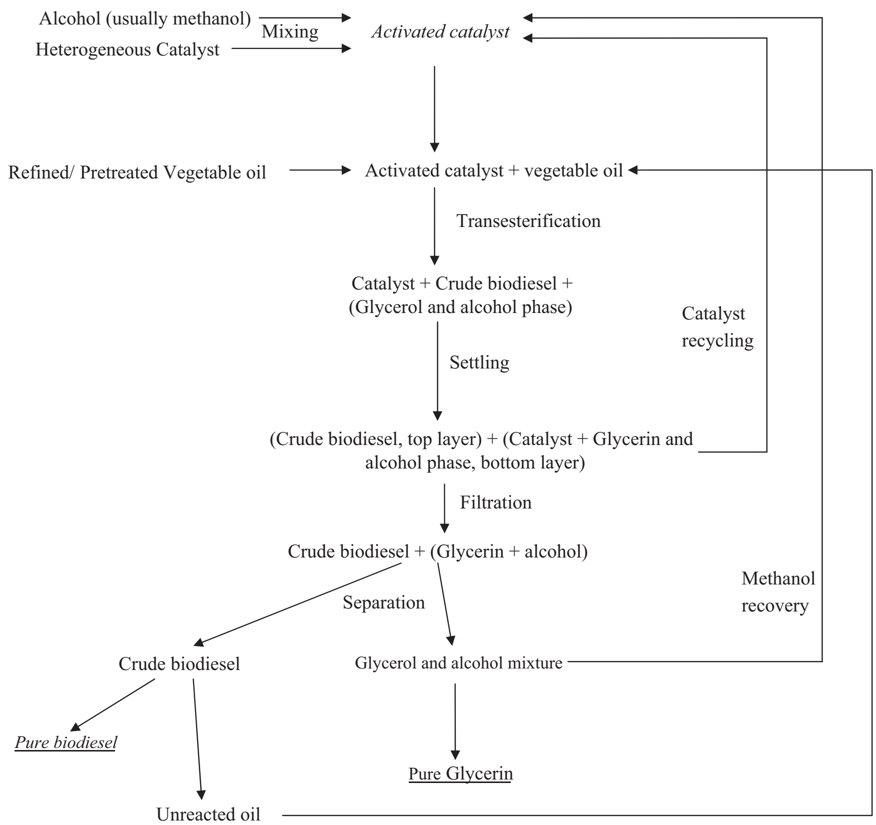


Fig. 2. Schematic block diagram of heterogeneous biodiesel production.

viability in biodiesel production, biodiesel manufacturers are focusing their attention towards heterogeneous catalysis and low -cost alternatives feedstock such as waste cooking oil and non-edible oil (such as Jatropha and Pongamia) [25,26]. As mentioned before, transesterification proceeds most efficiently on homogeneous base catalysts such as NaOH and KOH. However, due to some major drawbacks such as separation difficulty from product the focus is now on the development of heterogeneous catalysts which are easy to recover and could be reused for consecutive cycle. The schematic representations of biodiesel production with homogeneous and heterogeneous catalysts have been illustrated below Figs. 1 and 2). Table 1 below illustrates an overview on the different aspects of biodiesel production using different types of catalyst. The use of carbon based catalyst makes the biodiesel production even more environmentally benign. Fig. 3 represents the schematic for the preparation of carbon based catalyst from biomass and its utilization as a catalyst in biodiesel production. This demonstrates that the carbon based catalysts could not only reduce the cost of biodiesel making but also could be used as “green catalyst”.

1.2. *Carbon as catalyst*

Activated carbon (AC) also called activated charcoal, activated coal or carbo activatus is the most well known form of carbon as catalyst or catalyst supports. AC is a type of amorphous carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions [28].

Prior to its development as a catalyst/catalyst support, the earliest use of AC could be traced far back into the history of the Ancient Egyptians who utilized its adsorbent properties for purifying oils and medicinal purposes. Charcoal was used for drinking water filtration in ancient India and is still used. By the early 19th century both wood and bone charcoal were used in large-scale for the decolorization and purification of cane sugar. However, it was not until the beginning of the First World War that the potential of activated carbon was realized. During the 1939–1945 war, significant development took place – leading to the development of more sophisticated chemically impregnated carbon for the entrapment of both war and nerve gases. In the 19th century in Europe, powdered activated carbon was first produced commercially by wood as a raw material. In the United States, the first production of activated carbon used black ash as the source after it was accidentally discovered that the ash was very effective in decolorizing liquids [28,30–36]. Nowadays AC is mainly employed in filtering air and gases, wastewater treatment, removal of liquid-phase contaminants, including organic pollutants, heavy metal ions, organic dyes [29,30,32,37] and as catalyst support [40]. The application of these carbons has been considered as a major unit operation in chemical and petrochemical industries [29]. In addition to serving as an adsorbent, high porosity carbons have recently been applied in the manufacture of high-performance layer capacitors. Because of the introduction of rigorous environmental regulations and the development of new applications, the demand for porous carbons has increased [29].

The raw materials used for producing AC are materials with high carbon content (such as coal, wood, peat, coconut shells and petroleum residues [30,31]). These carbon-based materials are converted to AC by thermal decomposition in a furnace using a controlled atmosphere and heat by physical activation or chemical activation [32,33] involving the following steps: (1) removal of all water (dehydration), (2) conversion of the organic matter to elemental carbon, driving off the non-carbon portion (carbonisation) and (3) burning off tars and pore enlargement (activation) [34]. Activated carbons are divided into three categories based on their physical characteristics: (a) powdered activated carbon (PAC), (b) granular activated carbon (GAC) and (c) extruded activated carbon (EAC) [35]. The basic structural unit of activated carbon is closely approximated by the structure of pure

Table 1
An overview of biodiesel production by transesterification using different catalysts.

Type of catalyst	% Yield	Feedstock	Advantage	Disadvantage
Industrially used homogeneous alkali catalysts (NaOH, KOH)	96–98	Suitable for pretreated/refined vegetable oils	1. Very fast reaction	1. Requires refined or pretreated vegetable oils as feedstock (FFAs < 1 wt%) increasing the production cost
			2. Reactions occur at very mild conditions	2. Sensitive to water and FFAs can cause soap formation if too much catalyst is used. This decreases the biodiesel yield and causes problem during product purification especially while generating huge amount of wastewater
			3. Cheap and widely available (NaOH, KOH)	3. Catalyst cannot be reused
Heterogeneous alkali catalysts (CaO, ZnO, mixed oxides)	< 90	Suitable for pretreated/refined vegetable oils	1. Relatively faster reaction rate compared to acid catalyzed transesterification	1. Requires refined or pretreated vegetable oils as feedstock (FFAs < 1 wt%) increasing the production cost
			2. Reactions are less energy intensive and occur at mild conditions	2. Sensitive to water and FFAs can cause soap formation if too much catalyst is used. This decreases the biodiesel yield and causes problem during product purification especially while generating huge amount of wastewater
			3. Easy product separation by filtration	3. Leaching of catalyst active sites may result in product contamination
			4. Catalysts can be reused	4. Complex and expensive synthesis route
Homogeneous acid catalysts (H_2SO_4, HCl)	Upto 99	Suitable for waste and crude vegetable oils containing large amount of FFAs	1. Insensitive to FFAs and water content in the oil	1. Very slow reaction rate for transesterification compared to alkali catalysts
			2. Can simultaneously catalyze both esterification and transesterification reactions	2. Due to corrosive nature of acids like H_2SO_4, HCl especially designed reactors are needed to overcome the problem of corrosion on reactor and pipelines
			3. Preferable for low grade feedstock oil with very high FFAs content (e.g., waste cooking oil, crude non-edible oils)	3. Catalyst recovery is difficult
			4. No soap by-product is formed	4. Use of too much catalyst can increase the acid value of biodiesel, requiring extensive washings which generate huge amount of wastewater
				5. Requires high alcohol/oil ratio
Heterogonous acid catalysts (AC supported-SO_3H, SBA-15, HPA, etc.)	< 90	Suitable for waste and crude vegetable oils containing large amount of FFAs	1. Insensitive to FFAs and water content in the oil	1. Very slow reaction rate for transesterification compared to alkali catalysts
			2. Can simultaneously catalyze both esterification and transesterification reactions	2. Complicated and expensive synthesis routes in some cases
			3. Easy separation of catalyst from product and reusability	3. Energy intensive, requires high alcohol/oil ratio
			4. No soap by-product is formed	4. Leaching of catalyst active sites may result in product contamination
			5. Non-corrosive to reactor and reactor parts	
Enzyme (lipase)	99	Suitable for pretreated/refined vegetable oils as well as waste and crude vegetable oils containing large amount of FFAs	1. Insensitive to FFA and water content in the oil	1. Very slow reaction rate, even slower than acid-catalyzed transesterification
			2. Simple purification step	2. High cost, sensitive to alcohol, typically methanol that can deactivate the enzyme
			3. Mild reaction conditions and low alcohol/oil ratio	
Ionic liquids	–	Depends on the nature of IL used; for acidic, waste and crude oils or and for basic, refined or pretreated oils	1. Can act as both solvents and catalyst	1. Highly expensive
			2. Easy separation of products	2. Slow reaction rate compared to the conventional catalytic systems even for basic ionic liquids
			3. Depending upon its chemical properties, can act as both acid or base catalyst	3. Difficulty in separation of Ionic liquids and glycerin
Carbon based catalysts	< 90	Depends on the nature of the catalyst; for acidic, waste and crude oils or and for basic, refined or pretreated oils	1. Reusability	1. Slow reaction rate
			2. Simple synthesis route and inexpensive	2. Leaching
			3. High thermal stability	3. Use of High methanol to oil molar ratio
			4. Large surface area and uniform distribution of active particles	

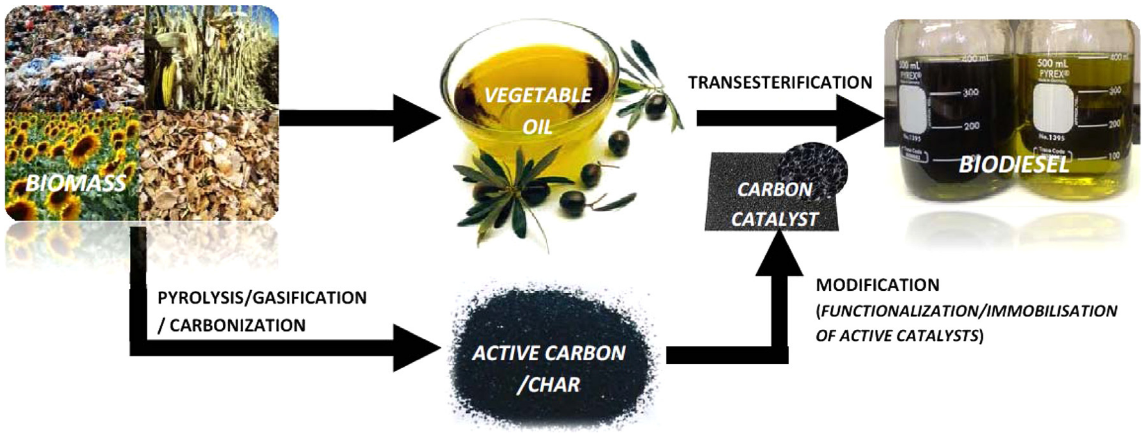


Fig. 3. Schematic representations for preparation of carbon based catalysts and its utilization for biodiesel production.

Table 2
Main features of different types of catalyst supports.
Adapted from http://www.jechem.co.jp/shirasagi_e/tech/catalyst.html, accessed on 6/3/2012 [101].

Carrier	Features
Activated carbon	Surface area: 800–1500 m^2/g. Heat stability
Alumina	Surface area: 100–300 m^2/g.
	Type α·γ·η are often used as carriers. Reasonable price.
	Heat resistance.
	Alkali resistance
Silica	Surface area: 200–600 m^2/g
Zeolite	Surface area: 350–900 m^2/g.
	Type A·X·Y·Mordenite·Erionite·ZSM-5 are often used as carriers.
	High controllability of pore size
Titania	Surface area: 40–100 m^2/g
Magnesia	Surface area: 50–200 m^2/g.
	Basicity.
	Strong adsorption of carbon dioxide and water in air

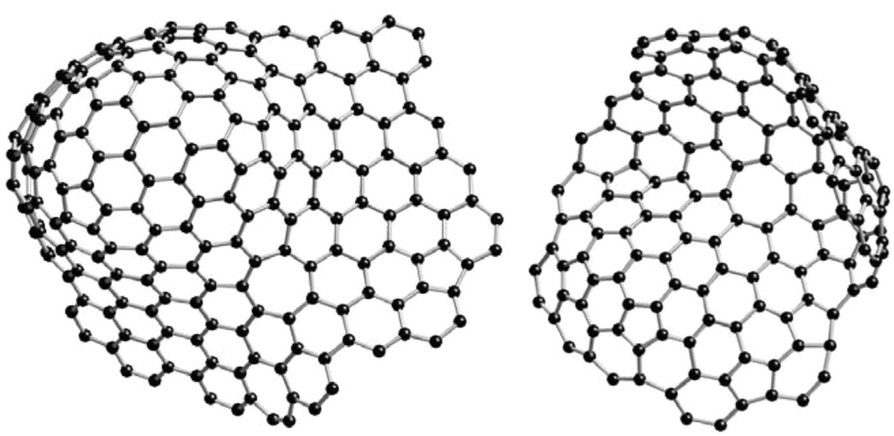


Fig. 4. Proposed structure of activated carbon.
Adapted from Harris et al. [38].

graphite. "Activated carbon is a crude form of graphite with a random or amorphous structure which is highly porous over wide range of pore sizes from visible cracks and crevices to cracks and crevices of molecular dimensions". Structurally activated carbon is a disorganized form of graphite due to impurities and the method of preparation (activation process) where the layers are held by carbon–carbon bonds. Its precise atomic structure, however, is unknown. A much more recent suggestion is that activated carbon has a structure related to that of the fullerenes, in other words that it consists of curved fragments containing pentagons and other non-hexagonal rings in addition to hexagons, as illustrated in Fig. 4. Such a structure would explain the microporosity of the carbon and many of its other properties [38].

Originally, catalytic activity of AC is due to its surface oxides and unique surface properties but its main use is in the form of a catalyst support. AC is a material that has all the required characteristics to be used as a catalyst support and additionally it has unique properties like its heat resistance, stability in both acidic and basic media, the possibility of easy recovery of precious metals supported on it and the possibility of tailoring both its textural and surface chemical properties. Table 2 presents a comparison of the properties of AC with the other commercially available support materials. It is well established

in the literature that the surface oxygen groups, which form anchoring sites for metallic precursors as well as for metals, dominantly determine the properties of activated carbon as a catalyst support material [1,3–6]. The acidic groups on the surface decrease the hydrophobicity of the carbon, leading to the accessibility of the surface to aqueous metal precursors [39]. The use of AC as a catalyst support has become popular during the last decade owing to its low material cost and desirable properties like very high surface area: 800–1500 m^2/g and thermal stability. Fig. 5 presents the total U.S. sales of catalyst support materials. Auer et al. published an excellent review on this topic [40]. Ni/Pd catalysts dispersed on AC supports are the most well known examples of such type of supported catalysts. The physical and surface chemical properties of AC can be modified via different procedures. It is evident from the literature that by changing the surface chemistry of AC support, (i) the dispersion of active metallic phase(s), (ii) the calcination/reduction properties of active metal(s) and (iii) the interaction between metals and extent of alloy formation for bimetallic catalysts can be modified [41,42]. Moreover, due to its close structural resemblance with graphite it is also possible to functionalise AC with groups like SO_3H, Ph-SO_3H, etc. similar to graphite, fullerenes, nanotubes or graphene [43–51]. This property was utilized by researchers to produce sulfonated-active carbons with –SO_3H groups. These sulfonated-ACs are amongst the most extensively studied AC-catalysts that are believed to substitute conc. H_2SO_4 in industries in the near future; they are reported to catalyze reactions like esterification, cellulose hydrolysis, nitration, transesterification, etc. by acting as a solid acid [22,48–64]. In addition there are numerous other reactions employing ACs as catalyst or catalyst support [40]. Biodiesel production is one such area where it has been suitably modified to serve as a catalyst.

2. Carbon-based catalysts in biodiesel production

In order to effectively cover the different types of carbon based (AC) catalysts reported in the literature for biodiesel synthesis, we have divided them into two categories: (i) functionalized catalysts (cover all types of AC catalysts where the active part is covalently attached to the support AC material) and (ii) supported catalyst (this category covers all the catalysts where porous carbon material or AC was used as a support for active catalysts such as CaO and KOH).

2.1. Functionalized catalysts

For simplification we further sub-divided Functionalized catalysts into two categories: (a) acid functionalized-ACs that include carbon catalysts where the active part is an acid or acidic functional group covalently attached to carbon material and (b) base functionalized-ACs that includes carbon catalysts where the active part is an acid or acidic functional group covalently attached to carbon material

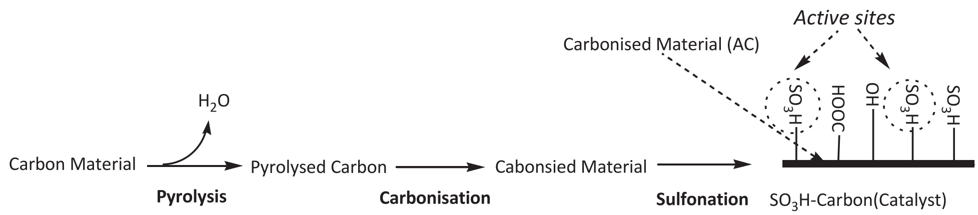
2.1.1. Acid functionalized-ACs

All the acid functionalized carbon catalysts reported in the literature for biodiesel synthesis are the sulfonated-ACs. They catalyze the formation of biodiesel (FAME) either by the esterification of FFAs (present in oil) or by simultaneously catalyzing esterification and transesterification reactions similar to conc. H_2SO_4 [59]. A number of papers reporting the use of such sulfonated-ACs with high density of sulfonic acid groups (–SO_3H) as a noble alternative to H_2SO_4 in reactions like hydrolysis, esterification, nitration are available [22,48–54]. Toda et al. reported the use of such a sulfonated-AC as an effective catalyst for biodiesel production by the esterification of vegetable-oils. In their study they partially carbonized D-glucose to obtain a rigid graphite like framework to which –SO_3H group was introduced by the sulfonation with conc. H_2SO_4 forming the reported SO_3H-sugar catalyst [21]. Based on this work researchers prepared similar sulfonated-carbon catalysts from different carbon precursors and utilized them as acid catalysts in biodiesel production. Basically there are two methods for the synthesis of sulfonated-carbon catalysts. They are (a) direct sulfonation (based on the method developed by Toda et al.) and (b) sulfonation via reductive alkylation/arylation.

2.1.1.1. Direct sulfonation. Sulfonated-ACs prepared by direct sulfonation are the most extensively studied among these materials. They have been prepared from different carbon sources (such as sugars, polycyclic aromatic compounds, polystyrene resins, activated carbon, biochar, and lignin) by individual researchers, but their preparation is based on the general scheme developed by Hara group (Scheme 2) [21,23,27]. Researchers have extensively studied the influence of different parameters like sulfonating agent, sulfonation time and carbon precursor on the activity of such catalysts.

In a typical process D-glucose or sucrose 10–15 g powder was heated for 15 h at 400 °C under N_2 flow to produce a brown–black solid. The solid was then powdered and heated in 200 mL of conc. H_2SO_4 (> 96%) or 150 cm^3 of fuming sulfuric acid (15 wt% SO_3) at 150 °C under N_2. After heating for 15 h and then cooling to room temperature, 1000 mL of distilled water was added to the mixture to form a black precipitate. The precipitate was washed repeatedly in hot distilled water (> 80 °C) until impurities such as sulfate ions were no longer detected in the wash water.

Catalytic activities of these materials (sulfonated-ACs) were examined in esterification of higher fatty acids at 80 °C in an ethanol–oleic acid mixture and ethanol–stearic acid mixture under Ar. Their results indicated that the sulfonated-AC prepared with fuming sulfuric acid showed higher acid site density (2.5 mmol/g total and 1.2 mmol/g SO_3H density). In comparison to typical solid acids such as Protonated Nafion, H-MOR and niobic acid ($N_2O_5 \cdot nH_2O$) sulfonated-ACs exhibited much higher activity even with their low surface areas (1 < to 2 m^2/g) resulting from the presence of abundant –SO_3H groups [21,53]. A similar method for preparing such materials by the incomplete carbonization of sulfonated polycyclic aromatic compounds in conc. H_2SO_4 was also developed by the same researchers [53,58]. Nevertheless, the aim of all reported methods in the literatures was to obtain a rigid graphite like network consisting of small polycyclic aromatic carbon sheets in a three-dimensional sp^3-bonded structure (structurally disorganized form of graphite) (Fig. 4). These graphite like materials can thereafter be functionalized/modified similar to graphite by schemes reported in the literature [47–51]. Sulfonation of such a material has been demonstrated to afford a highly stable solid with a high density of active SO_3H sites, which is physically robust and there is no physical leaching of SO_3H groups during use, therefore, such materials exhibit remarkable catalytic performance for the esterification of higher fatty acids [53]. In all cases, oxidation of the aromatic rings during sulfonation forms graphene carboxylate groups that stabilize the SO_3 amorphous carbon bearing SO_3H groups. Researchers have also proved that sulfonated-ACs contain Ph-OH, –COOH, and –SO_3H groups (Fig. 6) and therefore exhibit better catalytic performance during liquid-phase acid-catalyzed reactions compared to other solid acids [53,58]. Due to the formation of such groups on the carbon material during carbonization process they end up in the final product i.e. sulfonated-ACs. Their presence enhances catalytic performance by increasing overall acid density and by acting as sites for the attachment of substrates like triglycerides and fatty acids. The presence of these functional groups can be confirmed by Bohem titrations [60], cation-exchange experiments and elemental analysis. In a particular paper it was reported that the Hammet function of SO_3H groups in conventional sulfonated polystyrene-based resins is $H_0 > -3$. However, when prepared from sugar, the material has SO_3H groups with $H_0 = -8$ to -11, comparable to that of concentrated H_2SO_4 [64]. They attributed this strong acidity of the SO_3H groups in the presence of some SO_3H groups linked by hydrogen bonds, which



Scheme 2. Preparation of SO_3H-carbon.

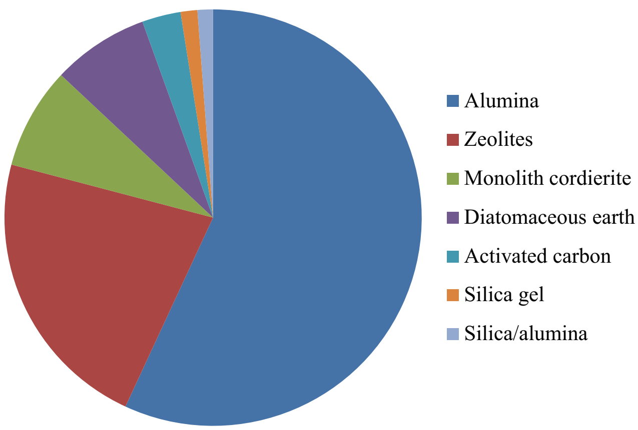


Fig. 5. U.S. sales of catalyst support materials. Adapted from Kemball et al. [102].

can result in strong acidity due to mutual electron-withdrawal. Such SO_3H-bearing amorphous carbons incorporate a large amount of hydrophilic molecules, including water, into the vacancies among the domains composed of graphene. The carbon material showed high catalytic performance as an efficient heterogeneous catalyst for biodiesel production by the esterification of oleic acid and transesterification of triolein. Transesterification in the presence of an adequate amount of water suppresses the formation of by-products. Under optimal conditions conversions up to 99.0% could be achieved for both esterification and transesterification reactions [22].

According to Zong et al., the activity of sulfonated carbon-based catalyst (D-glucose based) for the production of methyl ester is much higher than that of sulfonated zirconia which is one of the commonly used solid acid catalysts for biodiesel production. The main difference is attributed to fewer acid sites of sulfated zirconia compared to those of sulfonated carbon-catalysts [64].

However, when similar sulfonated catalyst was prepared from incompletely carbonized resins, amorphous glassy carbon, activated carbon, natural graphite exhibited no significant activity for esterification, hydration or hydrolysis. This was probably due to the compact carbon structure of these materials causing difficulty in sulfonation and due to the absence of surface functional groups leading to the lower acid density in the final sulfonated catalysts, suggesting that the catalytic activity of such catalyst is dependent on the type of carbon precursor used which can greatly influence surface area, formation of surface functional groups, structure of carbon framework and overall acid density [53,64].

The effect of carbon precursor on the activity of such novel catalysts was studied by Lou et al. using four different sources, namely D-glucose, cellulose, sucrose and starch for catalyst preparation. They observed that the best activity was exhibited by the starch catalyst which could give FAME yield of 95% compared to 88%, 80%, and 76% for cellulose, sucrose and D-glucose respectively, in 3 h. In all these carbohydrate derived catalysts the densities of –SO_3H group (1.47–1.83 mmol/g) were high despite the small surface area (4.1–7.2 m^2/g). The higher activity of starch derived catalysts was due to the high –SO_3H sites, slightly large surface area 7.2 m^2/g, pore volume and pore size compared to other catalysts. Due to large pore volume and pore size the starch derived catalysts were allowed for better interaction between the reactants and the SO_3H sites in the carbon bulk resulting in higher efficiency in catalyzing the esterification of higher fatty acids. The starch-derived catalyst was found to demonstrate the best reusability and retained about 93% of its original catalytic activity, even after multiple recycles, indicating the excellent operational stability. The reported high SO_3H densities were too much to be attributed to SO_3H groups attached to the catalyst surface via sulfonation [65]. Thus, researchers explained this behavior by suggesting that SO_3H groups in the amorphous carbon bulk (formed during carbonization) can also participate in the esterification, which was in agreement with the findings of Hara [22]. In their studies they reported that for starch derived catalyst carbonized at 400 °C, acid densities were the highest due to the formation of large amounts of surface functional groups (Ph-OH, –COOH, and –SO_3H) at that temperature, whereas at higher temperatures the formation of surface functional groups was reduced resulting in the decreased acid site densities and hence catalytic activity [65].

Similar catalysts were prepared by mixing glucose with sucrose, glutinous rice starch, corn starch and amylase as the starting material followed by pyrolyzing it at 400 °C for 60, 75 and 90 min resulting into the creation of polycyclic aromatic carbon rings. These rings are then incorporated with the SO_3H group by sulfonating the sample mixture with H_2SO_4 at 150 °C for 5 h. This catalyst was used for biodiesel production from waste cottonseed oil having high FFA of about 55.2 wt%. The authors have reported that glucose mixed with corn starch for 75 min could yield the best conversion of esterification owing to maximum acid densities. Further characterization of this catalyst has indicated that the composition of the catalyst is $CS_{0.073}O_{0.541}$ and it was composed of both Lewis acid sites and Brønsted acid sites caused by –SO_3H and –COOH. Although biodiesel yield of 90% was reported after 12 h using the glucose–starch mixture catalyst, it gets deactivated in consecutive cycles due to the loss of –SO_3H groups—which is a disadvantage. The catalyst was proposed to be regenerated by treating it with H_2SO_4 once again. Their research has shown that the final polycyclic aromatic carbon structure is affected by the amount of amylopectin content in starch [66].

In another study Mo et al. reported the synthesis of a sulfonated carbon composite solid acid (P–C–SO_3H) with three times higher acid density than the sulfonated-carbons prepared under identical conditions. It was produced by the simple pyrolysis of a polymer matrix impregnated with glucose followed by sulfonation. Structurally it was believed to have a flexible local structure of carbon network that closely resembles the structure of sulfonated sugars. The precursor of the composite catalyst P–C–SO_3H was prepared by adding drop-wise an aqueous solution of glucose (1.2 g glucose, 3 mL deionized water) and a small amount of concentrated sulfuric acid (~0.2 g) to pre-dried (100 °C air) Amberlite XAD1180 (a porous copolymer) to incipient wetness. This mixture was dried at 100–120 °C overnight and then pyrolyzed under dry N_2 at 300 °C for 1 h. The sugar catalyst (C–SO_3H) precursor was obtained by the pyrolysis of glucose under dry N_2 at

400 °C for 1 h. All the precursors were then sulfonated using concentrated sulfuric acid (1 g solid/20 mL H_2SO_4) at 150–160 °C for 13 h under a dry N_2 atmosphere. The resulting material was then washed with hot distilled water until no sulfate ions were detected in the wash water and dried at 100 °C. This catalyst exhibited higher acid site density (~3.6 times higher) and therefore improved catalytic activity for esterification activity of both small and large free fatty acids (acetic acid and palmitic acid). It also exhibited a better reusability than the sulfonated sugar catalyst C–SO_3H. The activity decrease of the C–SO_3H catalysts in the initial reaction cycles is due to the leaching of sulfonated polycyclic aromatic hydrocarbons, this phenomenon is not observed for P–C–SO_3H catalyst. Thus, P–C–SO_3H catalyst reported in the present study exhibits higher catalytic activity and better stability than C–SO_3H or P–SO_3H (sulfoanted polymer) at 60 °C [21,22]. 72.4% and 21.3% conversions of acetic acid and palmitic acid, respectively, were reported for the P–C–SO_3H catalysts in 1 h compared to 50.8% and 12.7% conversions for the C–SO_3H catalysts. The better performance of P–C–SO_3H was attributed to its higher SO_3H density of 2.42 mmol/g as opposed to the SO_3H density of 0.66 mmol/g for C–SO_3H catalyst. No significant deactivation was observed for P–C–SO_3H during six consecutive esterification cycles of acetic acid or palmitic acid with MeOH at 60 °C. Thus, the stable catalytic performance for P–C–SO_3H was attributed to the integrated carbon-polymeric matrix precursor. Elemental analysis also showed a negligible change in the S content of P–C–SO_3H. However, for C–SO_3H on the other hand, loss about 10% of the activity during three reaction cycles of acetic acid esterification that was observed due to the deactivation as a result of –SO_3H loss [27].

Shu et al. used vegetable oil asphalt and s-MWCNTs as carbon precursors to prepare similar catalysts. The authors reported that asphalt-based catalyst showed higher activity than the s-MWCNTs for the production of biodiesel. In their experiments the asphalt based catalyst showed higher activity even though it had a low surface area 7.48 m^2/g compared to the high surface area of 43.90 m^2/g. This was attributed to the high acid site density 2.21 mmol/g and loose irregular network and large pores present in the asphalt based catalyst which allows the diffusion of reactant easily into the internal acid sites than with the s-MWCNT catalyst. Even though the acid site density 3.09 mmol/g and surface area of 41.27 m2/g for the s-MWCNT catalyst were higher than the asphalt catalyst yet due to its smaller pores (average pore size of 7.48 nm); the entering of substrate molecules (cottonseed oil and methanol) was blocked from coming into contact with active $-SO_3$H groups located in the interior of the catalyst resulting in the reduced activity [67,68]. Overall these results were in good agreement with the work of Lou et al. where they showed that catalytic activity of such catalysts was primarily influenced by acid densities but not the surface area [65]. Upto 89.93% conversion of cottonseed oil was obtained (using the asphalt-based catalyst) when the methanol/cottonseed oil molar ratio was 18.2, reaction temperature at 260 °C, reaction time 3.0 h and catalyst/cottonseed oil mass ratio was 0.2%. Both catalysts demonstrated good reusability similar to other carbon based catalysts. In their studies 140 °C was reported to be a suitable reaction temperature for the esterification and 220 °C suitable to transesterification when such a carbon-based catalyst was used, respectively. TGA studies clearly indicated that the $-SO_3$H groups were stable at a reaction temperature up to 270 °C for both the catalysts [67–69]. These findings were in agreement with the results of TGA analysis carried out by Mo et al. for the analysis of a sulfonated glucose catalyst [27]. The authors further extended the study and compared activity of the vegetable oil asphalt catalyst with a petroleum asphalt based catalyst prepared by the same method. Their studies showed that the vegetable oil asphalt catalyst had higher acid site density 2.21 mmol/g and larger pore diameter 43.9 nm. Due to the high stability of its acid sites, loose irregular network, and the hydrophobic nature vegetable oil asphalt catalyst exhibited higher catalytic activity for biodiesel production from the model waste oil. The high acid density and pore volume were attributed to the loose irregular network structure of vegetable oil asphalt carbonized at 600 °C, than the more compact carbon structure of carbonized petroleum oil asphalt under similar conditions. Thus, the intercalation of concentrated H_2SO_4 with the carbon sheet of could be easier for carbonized vegetable oil asphalt leading to a higher degree of sulfonation. Researchers explained this behavior on the basis of chemical composition of starting materials. The main components of vegetable oil asphalt are straight chain aliphatic hydrocarbon polymers and that of petroleum asphalt are the heaviest hydrocarbons and the derivatives of non-metallic elements. Due to this difference they would have different pathways for the carbonization process. The derivatives of non-metallic elements are easier to carbonize to form graphitic carbon, so there was more graphitic carbon in the carbonized petroleum asphalt samples causing difficulty in sulfonation. The carbon-based solid acid catalyst prepared at carbonization temperature of 600 °C and sulfonated at 210 °C gave the highest catalytic activity for biodiesel production from the model waste oil. The use of higher carbonization temperatures of the catalytic activity decreased due to reduced acid densities as a result of formation of more difficult sulfonate graphitic carbons. The findings were in agreement with the previous works in the literature [22,67–69]. This solid acid consisted of a flexible carbon-based framework that supported highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups similar to the sugar catalysts reported earlier [22,27,64]. It could simultaneously catalyze transesterification and esterification, so it should potentially be useful for the conversion of waste oils with high FFAs concentrations to biodiesel [70].

Similarly Rao et al. prepared sulfonated carbon catalysts by employing de-oiled canola meal (DOCM) as precursor. They prepared the catalyst in four different ways which were—direct sulfuric acid treatment, partial carbonization of de-oiled canola meal at 400 °C followed by treatment with H_2SO_4, partial carbonization of de-oiled canola at 400 °C meal followed by steam activation and H_2SO_4 treatment and partial carbonization of de-oiled canola meal at 300 °C followed by treatment with H_2SO_4. They have reported that carbonization temperature greatly affects the acid site densities of the prepared catalyst. They observed that DOCM treated directly with sulfuric acid at 190 °C destroyed the major component of DOCM such as carbohydrates and proteins which lowered the acidity of the carbonized material. On the other hand new surface functional groups such as hydroxyl and aromatic structures are formed during the partial carbonization of DOCM which in turn reacts with sulfuric acid to form SO_3H functionalities on the surface of the catalysts. Hence the acidity in such a catalyst was higher compared to the direct sulfonated DOCM catalyst. The results indicated that the catalytic activity of the catalyst obtained by sulfonating de-oiled canola meal carbonized at 300 °C was the highest due to higher acid density and larger pores. The partial carbonization at 300 °C retained more functional groups, which upon sulfuric acid treatment produced more acidic functionalities on the surface of the catalyst. These findings were similar to the previous works where maximum catalytic activities were reported when carbonization temperatures were kept between 400 and 600 °C. The prepared catalysts were physically stable up to 250 °C, as evidenced from the results of TGA analysis. Maximum conversion up to 93.8% of waste canola oil was achieved with this catalyst under optimal conditions of reaction temperature, reaction time, molar ratio of substrate to methanol and catalyst concentration of 65 °C, 24 h, 1:60 mol/mol and 7.5%, respectively [71].

Pua et al. also prepared a similar solid acid catalyst from Kraft lignin by its chemical activation with phosphoric acid, followed by pyrolysis and H_2SO_4 treatment. It exhibited an activity similar to the other sulfonated-carbon catalyst such as sugar, biochar derived

catalysts [22,45]. The lignin derived catalyst had a very high surface area 54.8 m^2/g and total acidity of 0.74 mmol/g measured from NH_3 TPD, and the catalyst could be reused up to three times with little deactivation under optimized conditions. The catalyst was successfully employed in one step biodiesel production from crude Jatropha oil with very high acid value 12.7 mg KOH/g and very high (FAMEs) yield (96.3%) was achieved in 5 h under optimal conditions [72].

Recently, a biomass pyrolysis by-product, biochar, has gained immense attention as a potential precursor for AC. Structurally AC and biochar are very similar, but due to their low porosity and adsorptive properties resulting from the presence of impurities it cannot be directly used as a catalyst/catalyst support. Therefore, it is conveniently converted to AC, by physical or chemical activation [73]. The preparation of similar carbon catalysts using biochar as the starting carbon material has been reported. Dehkhoda et al. sulfonated commercial biochar obtained from three different sources according to Scheme 2 with two different sulfonating agents (conc. H_2SO_4 and fuming H_2SO_4) to produce sulfonated-biochars catalysts [22,58,61]. The effect of chemical activation on catalyst activity was also investigated. Surface area of the biochar was increased by chemical activation using 10 M KOH through porosity development. In a typical process concentrated sulfuric acid was added to 20 g of biochar (both activated/unactivated) in a 500 mL round bottom flask. The mixture was heated to 150 °C with a heating mantle and monitored with a temperature controller and corrosion resistant Type-J thermocouple for 24 h. After heating, the slurry was placed in cool distilled water and filtered. The biochar catalyst was washed with hot (< 80 °C) distilled water until wash water was neutral and free from sulfate ions. Following filtration, the biochar was dried in an oven at 70 °C for approximately 1 h. The effect of different parameters such as chemical activation, sulfonating agents, sulfonation period on acid site density and catalytic activity was investigated. The activities of these catalysts were tested in transesterification of vegetable oils and the esterification of FFAs. The studies showed that the use of longer sulfonation period and stronger sulfonating agents produced more active catalysts with higher acid densities. Biochar samples sulfonated with conc. H_2SO_4 produced acid catalysts with strengths comparable to sulfated Zirconia while the use of fuming sulfuric acid produced catalyst with much higher acid site densities. It was also reported that only the biochar was sulfonated using fuming H_2SO_4 and use of a higher (acid/char ratio) during sulfonation showed activity in transesterification owing to the higher $-SO_3H$ densities (2.5–3.2 mmol/g) and were more effective in esterification reactions as well. The transesterification activity was found to increase as a result of increased surface area due to (KOH activation) and $-SO_3H$ densities. Overall the catalytic behaviors of biochar catalysts were found to be related to sugar-catalysts [74]. However, the maximum yield obtained for transesterification was still as low as ~10%. Based on these results further investigations on the development of surface area and the catalytic activity for transesterification and carbon structure were conducted by the same authors. In this study they used biochar generated from the fast pyrolysis of woody biomass (a mixture of wood waste, white wood bark and shavings) as starting materials and carbonized it at different temperatures (450, 675, and 875 °C) following chemical activation with KOH for 2 h. Their results showed that with an increase in carbonisation temperature the BET surface area and pore volume increases, but acid density of the catalyst decreases similar to the sulfonated catalysts reported previously [64–66]. This is because at higher carbonisation the aromaticity and graphitic carbon content in the carbon material increases and it becomes difficult to sulfonate such a material. The increased surface area is due to the increased porosity of the material. The effect of carbonisation temperature of acid site density and catalyst activity is shown in Table 3. The results indicate that char activated at 675 °C produced the most active catalyst due to a combined effect of large surface area and high SO_3H density (44.2% conversion of canola oil). Structurally the sulfonated-biochar catalyst resembled other sulfonated carbon catalysts (obtained by carbonisation of cellulose, D-Glucose, carbohydrates, etc.) [22,64,67]. The catalyst demonstrated poor reusability due to the loss of active $-SO_3H$ groups from the catalyst surface similar to carbon catalysts [64,66]. The deactivation of biochar catalyst was more rapid compared to the sugar, asphalt or s-MWCNT catalysts due to the easier leaching of $-SO_3H$ groups located on the carbon surface whereas the low leaching observed in sugar, asphalt catalysts were due to the presence of the active $-SO_3H$ groups inside the bulk [23].

Table 3
Effect of char activation temperature on properties and yield of sulfonated-biochar catalysts.
Adapted from Yu et al. [23].

Char activation temperature (°C)	BET surface area (m^2/g)	Total acid density (mmol/g)	SO_3H group density (mmol/g)	% Yield
450	1.88	2.6 ± 0.1	0.839	7.6 ± 0.6
675	640	1.2 ± 0.1	0.405	18.9 ± 0.6
875	1411	0.43	0.377	8.4 ± 0.3

A comparative study of similar sulfonated-ACs prepared by sulfonating biochar and wood based AC was conducted recently by Kastnera et al. The catalysts were prepared by the same scheme used by Dehkhoda et al., additionally they studied the effect of O_3 treatment on carbon structure and catalyst activity, by sulfonating O_3 treated biochar under identical conditions (O_3 is reported to cause pore expansion and increase in surface area). Studies with different sulfonating agents showed that the use of stronger sulfonating agents produced catalysts with higher acid densities in agreement with the findings of Dehkhoda et al. [23,74]. According to the Kastnera et al. the wood based AC was difficult to sulfonate due to the higher aromaticity and graphitic carbon content in the material. However, using stronger sulfonating agent (solid SO_3) it was possible to obtain very high acid densities even for activated carbon. The catalytic activity was examined in the esterification of higher fatty acids (palmitic and stearic acids). In their study the wood based AC catalyst prepared by sulfonating with (solid SO_3) showed the highest activity due to the combined effect of high acid density, particle strength, hydrophobicity and large surface area. The surface area 338 m^2/g reported for the sulfonated-wood AC in this study was by far the highest for such types of catalyst. This showed that catalytic activity was also influenced by surface area along with acid site density and pore size similar to the findings of the Dehkhoda et al. However, there was the loss of activity upon reuse due to water absorption and $-SO_3H$ leaching reflected by a decreased surface area 338–1.2 m^2/g and reduced acid density 0.86–0.62 mmol/g similar to the other sulfonated-ACs [75].

Arancon et al. by carbonization and sulfonation (conc. H_2SO_4) of corncobs in a two step process also produced similar sulfonated-ACs. Effects of carbonization temperature showed good agreement with the previous results and the use of 600 °C produced catalyst with the highest SO_3H density (0.14–0.15 mmol/g) and activity due to the combination of high surface area and high acid site density. TEM micrographs (Fig. 7) of selected carbonaceous materials demonstrated the typical amorphous structure of the carbonaceous materials, with the high temperature carbonized samples showing a structure close to graphite-type materials. From their results, no significant influence of the carbonisation time (5–10 h) on catalytic activity was found whereas a marked effect of carbonisation temperature on activity was observed. FAME yield up to 98%

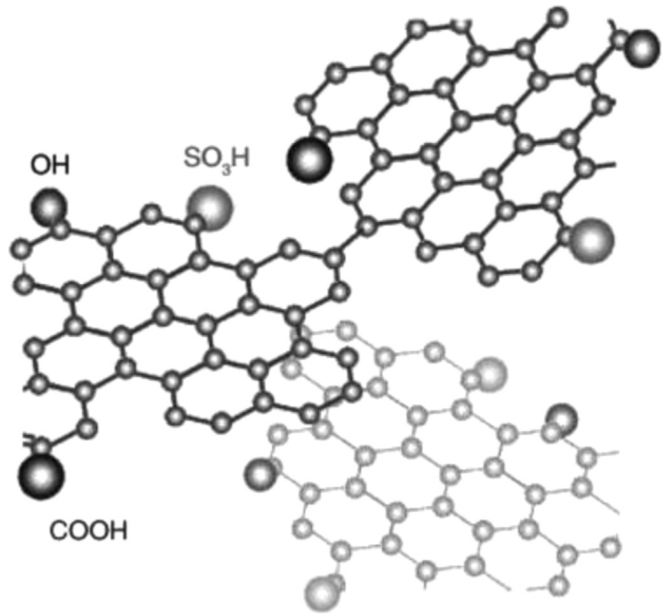


Fig. 6. Proposed schematic structure of the sulfonated carbon materials.
Adapted from Okamura et al. [53].

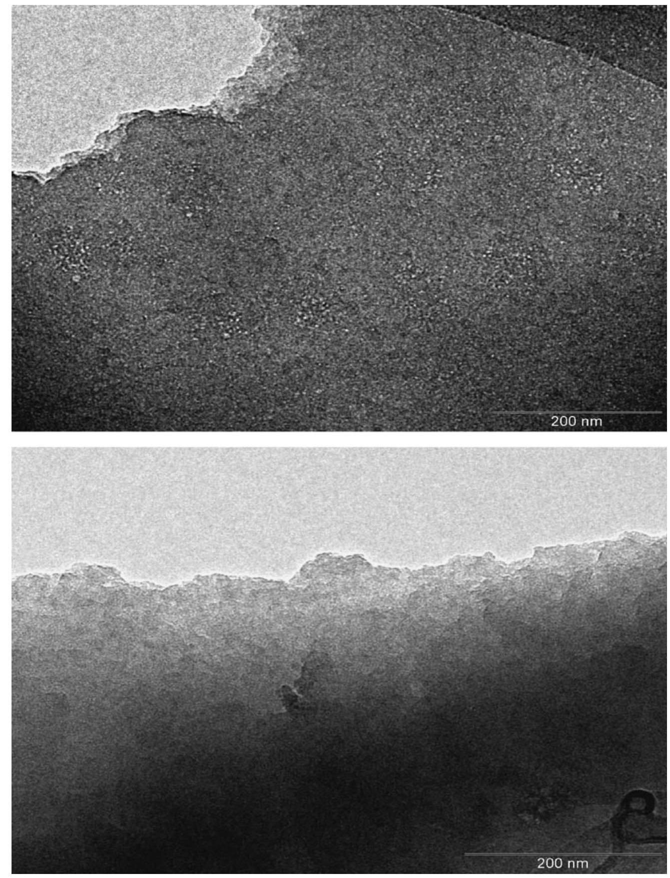


Fig. 7. TEM micrographs of selected sulfonated carbonaceous materials obtained from corncob (top carbonized at 600 °C) and (bottom carbonized at 400 °C).
Adapted from Arancon et al. [76].

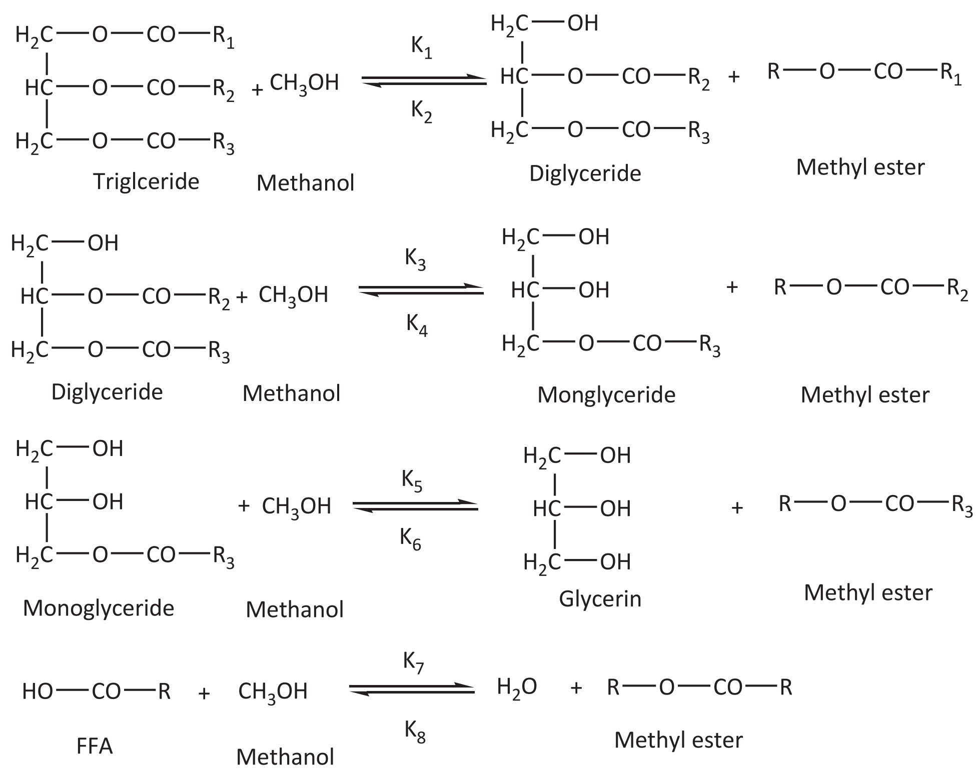
was obtained with the use of 32:1 MeOH/oil ratio, 3 wt% catalyst, in 6 h and 80 °C for feedstock oil 12 wt% FFAs with the optimum catalyst. The reusability and stability of the material was also investigated under the same conditions. For this purpose, the solid acid catalyst was filtered off upon reaction completion, washed and oven dried overnight at 100 °C prior to its reuse in the process. The material showed strong deactivation at each cycle and almost completely lost its activity after two reuses (17% conversion). The severe deactivation was attributed to the removal of the active $-SO_3H$ groups upon recycling (washing/drying) and poisoning due to the impurities present in the waste oils similar to the biochar catalysts [23,75]. Hot filtration tests showed that the filtrate (upon catalyst separation) did not further react, meaning that deactivation was mainly due to the loss of $-SO_3H$ during catalyst washing [76].

Devi et al. recently proposed a new one step method based on the in situ partial carbonization and sulfonation of glycerol (a by-product from biodiesel production) to develop similar solid acids. This novel idea casted new light both on the utilization of glycerol and on the development of new carbon based solid acid catalysts for biodiesel production. In conventional method (Scheme 2) the catalyst is prepared in two steps. In the first step, the biomass, such as sugar and starch, is incompletely carbonized to form the polycyclic aromatic carbon sheets. Then the sulfonation of the incomplete carbonized materials is taken into action as the second step [22,64,65]. However, the sulfonation is carried out with a large amount of sulfuric acid at high temperature under inert atmosphere, which is not an environment-friendly process. This new carbon catalyst showed very good water tolerance and reusability, which is useful for the preparation of biodiesel from fatty acids or from fatty acids present in vegetable oils and animal fats. The acidity of the catalyst was found to be in the range of 1.6–4.6 mmol/g [77,78]. Its structure and morphology was found to be related to the sugar and biomass derived catalysts according to the results of XRD and SEM analysis. A mesoporous structure was confirmed by N_2 adsorption isotherm and pore size distribution, leading to a high BET surface area of 87 m^2/g, higher than the sugar and biochar based catalysts discussed earlier. The mesoporous structure and morphology favored the catalytic activity for the production of biodiesel. The glycerol derived catalyst showed better reusability than the previously discussed sugar and biochar catalysts [22,64,65]. It was also reported that the catalytic activity could be maintained with over 95% conversion even after five runs, indicating the higher stability of the catalyst. Furthermore, TGA results showed high thermal stability and showed that it could maintain its structure up to 260 °C [78].

Guo et al. used lignin-derived from nutshells of *Xanthoceras sorbifolia* (an oil plant in China) to prepare similar sulfonated carbon catalyst in a one-step method involving simultaneous carbonisation and sulfonation at 150 °C. The catalyst exhibited high esterification activity with the maximum free fatty acids (FFAs) conversion (up to 97%) under optimal conditions. It demonstrated reusability up to three times and structurally resembled the sulfonated carbon catalyst prepared by the conventional two step method (Scheme 2) by carbonizing the lignin at 400 °C [79].

Chang et al. very recently prepared a highly active, robust and reusable sulfonated carbon catalyst for synthesis of biodiesel; it was prepared by the sulfonation of a carbonized mesoporous phenolic resin with concentrated sulfuric acid. The influence of carbonization temperature on the pore structure and acidity showed that the sulfonated catalyst carbonized at a low temperature (400 °C) showed the highest acidity of 2.21 mmol H^+/g and activity, meanwhile, retaining a mesoporous structure and relatively large surface area of the catalyst that exhibited high reusability up to five cycles [80].

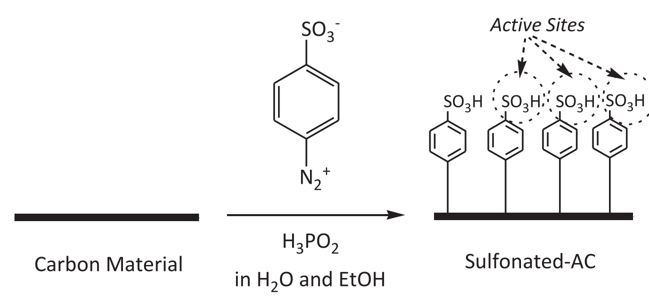
Apart from the studies on the structural characterization and the use of carbon based solid acids, a kinetic study on solid acid catalyzed simultaneous esterification and transesterification of vegetable oils was also conducted. To study the reaction kinetics a simplified kinetic model based on the reaction Scheme 3 was proposed. The kinetic model was validated for two different



Scheme 3. Proposed reaction scheme for simultaneous esterification and transesterification.

carbon catalysts obtained by the sulfonation of carbonized vegetable oil asphalt and petroleum asphalt. The results were in agreement with the experimental data and all the forward and backward reactions that followed the 2nd order kinetics and rate constants obeyed Arrhenius equation. In their experiments, the overall reaction was established to be a pseudo homogeneous in nature. Studies on particle size (in the range 60–160 μm) and agitation speed (in the range 180–300 rpm) showed no effect on overall rate of the reaction [81].

2.1.1.2. Sulfonation by reductive alkylation/arylation. A number of methods for efficient modification/functionalization of carbon surfaces are available. These include grafting through electrochemical, chemical reduction of aryl diazoniums, reductive alkylation and arylation, condensation [43,44,49–51,82,83] and so on. Sulfonation of carbon surfaces by reductive alkylation/arylation of sulfonic acid-containing aryl radical has been used exclusively by researchers to prepare sulfonated-ACs using various carbon sources such as ordered mesoporous carbon (OMC), nanotubes, graphite, and graphene according to Scheme 4 [45–47,55]. The resulting materials were employed as solid acids in reactions like hydrolysis, esterification, etc. However, only a limited number of papers reported the synthesis and use of such sulfonated-ACs. Based on Scheme 3, Wang et al. reported the synthesis and use of sulfonated-OMCs in biodiesel synthesis and hydrolysis. Sulfonic acid functionalized OMCs were synthesized by the covalent attachment of sulfonic acid-containing aryl radical and on the surface of mesoporous carbons using H_3PO_2 [55,62]. OMC was synthesized from SBA-15 via Template-Mediated Structural Transformation [84]. The alumina templates were mixed and thoroughly ground with resorcinol; the mixture was transferred to a round bottom flask containing 30 mL of mesitylene, 2.5 mL of furfural and 3 drops of 1,2-ethylenediamine. After stirring at 90 °C for 4 h, the alumina/resorcinol–furfural resin composite was filtered, washed with ethanol three times and dried in an oven at 130 °C.



Scheme 4. Covalent attachment of Ph-SO_3H on carbon surface.

To obtain the mesoporous carbon, the composite was carbonized under N_2 for 3 h and then immersed in a 24% hydrofluoric acid (HF) solution at room temperature for 3 h to dissolve the alumina.

The prepared sulfonated-OMCs exhibited high acid densities 1.95 mmol/g comparable to the sulfonated-ACs [22,23,27,55]. Through the combination of the advantages of carbon-based framework (high thermal stability) and the unique features of OMCs (large surface area, uniform porosity) the resulting materials showed higher activity for acid-catalyzed biodiesel reaction compared to the other solid acid catalysts. High conversion up to 73.59% was achieved under optimized conditions. The high acid density and hydrophobic surface property of SO_3H–OMC make it a highly efficient biodiesel catalyst. Large pore size favored the diffusion of large organic molecules which contributed to the enhancement of catalytic ability. The SO_3H–OMC exhibited a better reusability compared to sulfonated-AC as catalysts. It could be reused several times without any noticeable loss of activity due to the high stability of the covalently attached Ph-SO_3H groups which was not observed for directly sulfonated-ACs [62]. These modified carbons were shown to possess high surface area (~1000 m^2/g), a bimodal pore size distribution and high strong

acid density (1.86 mmol H^+/g). The efficient catalytic ability was attributed to the high surface area and a proper mesopore texture. Further investigations were made on the effect of texture, carbonization temperature on the activity of carbon-based catalysts by Geng et al. [85]. The texture of Ph-SO_3H-modified carbon catalysts was tuned using three types of alumina templates (AI, AII and AIII) with different porous structures with slight modification in the sulfonation process which was carried spontaneously (without addition of H_3PO_2). Results showed that the use of different templates led to carbon catalysts with different textures (pore sizes and surface area) which in turn affected the activity. To investigate carbonization influence, resorcinol–furfural resin was carbonized under N_2 gas at 500–1000 °C using AI as the template. As, the carbonization temperature directly determines the amount of oxygen-containing groups (e.g., –OH and –COOH) on the carbon matrix. Increasing the carbonization temperature eliminated these groups and increased graphitic carbon content to some extent as indicated by the atom ratios of carbon to oxygen. When the temperature was higher than 700 °C, however, the reduction of oxygen content was not clear, and the carbon content of C-AI-900 (92.56%) and C-AI-1000 (92.88%) was almost identical. Therefore, 700 °C was concluded to be the optimal carbonisation temperature. The optimal catalyst, SC-AI-900, carbonized at 900 °C displayed much higher activity than the traditional solid acid catalyst Amberlyst-15 (a rate constant of 1.34 h^{-1}, three times that of Amberlyt-15, and a TOF of 128 h^{-1}, eight times that of Amberlyst-15). In addition, it could be easily separated from the reaction system by filtration and reused. There was no distinct activity drop due to the recycling after the initial deactivation, clearly suggesting that Ph-SO_3H-modified OMC is a stable and efficient solid acid catalyst. Therefore, such carbon-based solid acids could also be useful for many other acid-catalyzed reactions involving large reactant molecules [85]. Sulfonation by reductive alkylation/arylation of sulfonic acid containing aryl radical is more preferable due to higher yields, use of mild reaction conditions and no structural alteration/changes in the structure of carbon framework following sulfonation which is crucial in order to preserve the high surface area and the porosity of carbon material. Use of this method ensures complete covalent attachment of acidic Ph-SO_3H groups on the carbon framework unlike the previously discussed direct sulfonation method.

2.1.2. Base functionalized-ACs

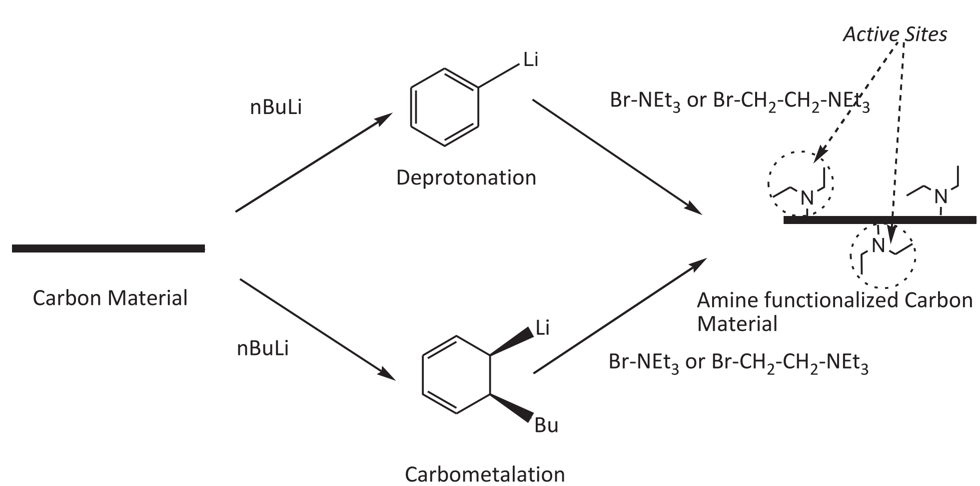
Very limited amount of work is available in the literature dealing with base functionalized-ACs.

Tessonnier et al. in a recent work used N-bases grafted to multiwalled carbon nanotubes (MWCNTs) as a solid base. Various amino groups (1°, 2° and 3°) were grafted onto the surface of MWCNTs using the scheme shown in Scheme 5.

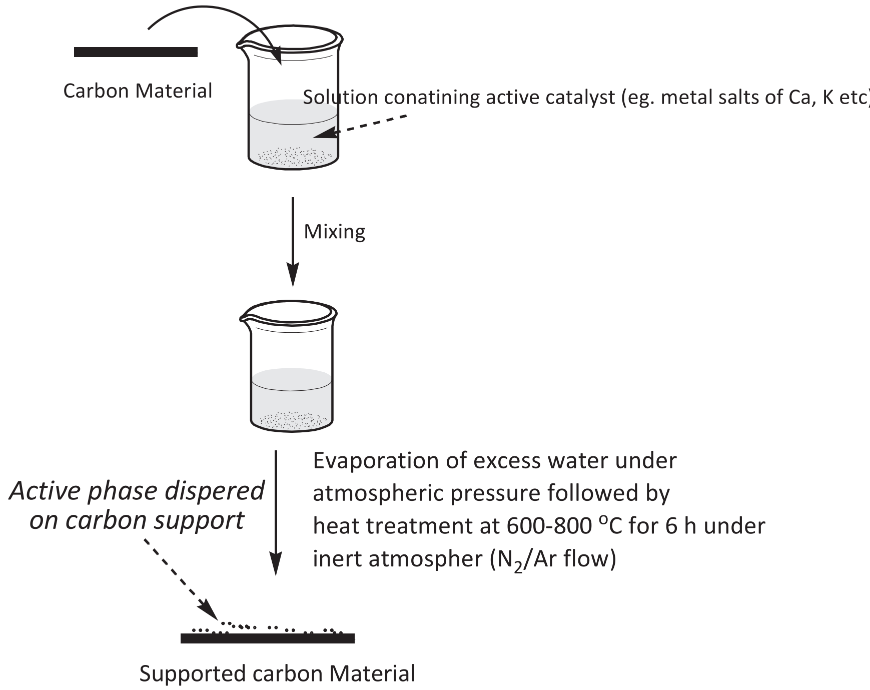
Yuan et al. also prepared amino-grafted graphene using the same scheme. The prepared materials were employed as metal-free solid base catalysts in reactions like transesterification and hydrolysis of ethyl acetate. Specifically, the amino-grafted multi-walled carbon nanotubes (N-MWCNTs) were used as an effective base catalyst in transesterification of triglycerides (glyceryl tributyrate). In their studies, all the amino grafted nanotubes were found to be basic in nature (pH > 7). The nanotubes grafted with 3° amines (Et_3N-CNTs) were found to be the most basic (basic site density of 1.00 mmol/g and pH = 10.30) and hence the most active in the transesterification of triglycerides. The higher activity was due to the higher basicity of 3° compared to the 2° and 1° amines. The materials also exhibited a good thermal stability, nanotubes grafted with 3° amine exhibited the highest stability up to 130 °C while 2° amine grafted amine was found to be the least stable. The catalyst showed good thermal stability. Reusability tests that were performed showed strong deactivation of the catalyst due to the adsorption of the triglycerides on catalyst surface (indicated by reduced basic site density 0.96 mmol/g) but no significant leaching of amino groups was observed. The authors suggested washing and regeneration of the catalyst with methanol to overcome this limitation. Under optimal conditions the highest conversion of 77% was reported for Et_3N-CNTs, better than hydrotalcite tested under similar reaction conditions [86–88]. However, tests with vegetable oils and long chain triglycerides are still required.

2.2. Supported catalysts

Apart from the sulfonated-AC catalysts, the use of porous carbon as a support for active catalysts like CaO, KOH, 12-tungstophosphoric acid (TPA), etc. was also investigated by different researchers. Zu et al. used different types of porous carbon materials, such as carbon molecular sieves (CMS), active carbon (AC), and nanoporous carbon (NC-2) 42 and CMK-3, as supports for the preparation of supported CaO catalysts by incipient-wetness impregnation of aqueous solutions of the corresponding $Ca(NO_3)_2$ precursors on the different carbon supports (Scheme 6). All the carbon-supported CaO catalysts were found to be active as solid-base catalysts for the transesterification of triacetin with methanol. In particular the CaO supported (NC-2) was found to be the most effective. The catalytic performance was influenced by a variety of factors, such as the nature of carbon supports, the concentration of impregnated CaO, the heat treated temperatures of the catalysts, and the reaction temperatures. These carbon supported CaO catalysts showed better performance than SBA-



Scheme 5. Grafting of amines onto carbon surface.



Scheme 6. Preparation of carbon supported catalysts.

15-supported CaO due to features like large surface area, pore volume, etc. (NC-2) supported catalyst displayed good reusability, which is due to the presence of abundant oxygen-containing functional groups on the surface of this material which were thought to act as anchoring centers for the active CaO phase. These centers resulted in the formation of a stable linkage between CaO species and the NC-2 support [89].

Zu et al. in an another study used graphite oxide (GO), a layered and oxygen-abundant material produced by the controlled oxidation of graphite as a support material for CaO. Graphite oxide (GO) supported CaO catalyst was prepared according to the conventional incipient-wetness impregnation of aqueous solutions of the corresponding $Ca(NO_3)_2$ precursors on GO and GO-T support (GO with a reduced number of oxygenated functional groups). The resulting material CaO/GO was successfully applied to the transesterification of soybean oil with methanol. Uniform dispersion of the CaO particles on the surface of the graphite oxide sheets of fresh and used CaO/GO catalysts were observed in the TEM images. High BET surface area of 437 and 439 m^2/g, and similar average pore sizes of 10.7 and 10.0 nm, respectively, were observed for CaO/GO and CaO/GO-T catalysts. CaO/GO and CaO/GO-T were found to be good catalysts for the transesterification of soybean oil with methanol with FAME yield reaching $<97\%$, after 2 h. The oxygen-containing groups on the surface of GO are likely effective anchoring centers for the active phase, thus resulting in the formation of active and stable GO-supported CaO catalyst for the transesterification reaction. Multiple transesterification reaction cycles were also carried out to examine the recyclability of the CaO/GO and CaO/GO-T catalyst. CaO/GO could be reused up to 4 cycles with no significant loss of activity. However, CaO/GO-T showed poor reusability due to the leaching of CaO particles as confirmed by hot filtration test, it was also reflected by the reduced FAME yield: 18.6% after 4 h upon reuse. Observed leaching was attributed to the absence of enough oxygen containing anchoring sites in GT-O support. Transesterification in the presence of CaO/GO was similar to that in the presence of CaO/NC-2 [89], but the two catalysts differ in the temperatures required for regeneration. While CaO/NC-2 had to be heat treated at 1073 K, CaO/GO could be regenerated at 873 K [90]. These findings confirm that the presence of oxygen-containing anchoring groups on the surface of carbon support is crucial for the formation of active and stable carbon supported CaO catalyst. Such carbon supported catalysts successfully address all the major problems like low surface area, sensitivity to the presence of water and leaching by polar species (e.g., glycerol, water) associated with CaO catalyst employed usually in biodiesel synthesis.

Konwar et al. reported an active carbon supported CaO catalyst prepared entirely from waste biomass. In their study both the active phase (CaO) and support (AC) material for the catalyst were prepared from waste shells of *Turbonilla striatula* (TS). To prepare the support material shells were carbonised and activated with KOH under N_2 flow, in the next step The AC was mixed with grounded and dried shells of TS followed by calcinations at 900 °C for 3 under N_2 flow to obtain the catalyst. It exhibited high basicity ($15 < H_0 < 18.4$) similar to pure CaO and specific surface area of 84 m^2/g and improved water tolerance. Under optimized conditions very high methyl esters yields up to 96% were obtained in the transesterification fried soybean oil [91].

Similarly, Baroutian et al. also reported the efficient immobilization of KOH on palm shell AC and its utilization as a catalyst in transesterification of palm oil. AC particles were agitated in an orbital shaker with KOH solutions (0.025–0.500 g/mL) and dried to produce the supported KOH/AC catalysts. The reduced surface area of KOH/AC catalyst from almost 1000 m^2/g (AC) to 214.46 m^2/g (KOH/AC) indicated filling of KOH molecules into the AC pores. The highest yield 97.72% was reported at 64.1 °C temperature, with 30.3 wt% catalyst loading and 24:1 methanol/oil molar ratio. The KOH/AC catalyst could be reused up to three times maintaining up to 90.6% of its original activity. This decay was accounted to the leaching of active sites to the reaction media due to the weaker interaction between the potassium species and activated carbon surface when compared to carbon supported-CaO catalysts [92]. KOH/AC catalyst when employed in a tubular ceramic (TiO_2/Al_2O_3) packed bed membrane reactor could give 94% conversion of palm oil at 70 °C reaction temperature, 157.04 g catalyst per unit volume of reactor and 0.21 cm/s cross flow circulation velocity. Under

Table 4
Comparison of the features and performance of all the major carbon-catalyst used in biodiesel synthesis.

Catalyst	Reaction conditions					Conversion/ yield	Advantage	Disadvantage	Ref.
	Temperature (°C), others	Amount and type of alcohol	Vegetable oil/ triglyceride	Catalyst loading	Reaction time (h)				
Functionalized carbon catalysts									
Acid functionalized carbon catalysts									
Sulfonated, carbonized cellulose	130,700 kpa	MeOH=3.8 g, triolin=1.7 g,	Triolin	0.4 g	5	98.1%	1. Higher activity than Amberlyst-15, Nafion NR50, sulfonated active carbon (commercial) 2. High acid site density 3. Effective in transesterification and esterification	1. Reusability, (leaching of active SO_3H) 2. High MeOH:oil ratio	[22]
Sulfonated, carbonized D-glucose	80; reflux system	Fatty acid=10 mmol, MeOH =100 mmol	Palmitic acid/oleic acid/ stearic acid	0.14 g	5	$\geq$95%	1. Higher activity than Amberlyst-15, sulfated zirconia and niobic acid 2. High acid site density	1. Less active in transesterification 2. Reusability (leaching of active SO_3H)	[59]
	80; reflux system	MeOH =5.54 g, oil=5.0 g	Waste oil (27.8% FFAs)	0.5 g	15	>90%	3. Effective in esterification	3. High MeOH:oil ratio 4. Slow reaction	
Sulfonated, carbonised D-glucose impregnated with polymer matrix (Amberlite XAD1180)	60	MeOH:acetic acid molar ratio=2	Acetic acid	3 wt%	1	72.4%	1. Improved reusability 2. Higher acid site density than sulfonated-sugar catalysts 3. Effective in simultaneous esterification and transesterification	1. Slow reaction	[27]
	60	MeOH:oil molar ratio=6	10% palmitic acid in soybean oil	2 wt%	1	21.3%			
Sulfonated-MWCNTs	240	MeOH:oil molar ratio=18.2	Cottonseed oil	0.2 wt%	2	84–85%	1. Good reusability 2. Effective in esterification	1. Very high temperature 2. High MeOH:oil ratio	[67]
Sulfonated-carbonized vegetable oil asphalt	260	MeOH:oil molar ratio=18.2	Cottonseed oil	0.2 wt%	3	89.93%	1. Good reusability 2. Effective in esterification	1. High temperature 2. High MeOH:oil ratio	[70]
Sulfonated, carbonized petroleum asphalt	220	MeOH:oil molar ratio=20.9	Model waste oil (50% cottonseed oil and 50% oleic acid)	0.3 wt%	3	$\leq$84%	1. Good reusability 2. Effective in esterification	1. High temperature 2. High MeOH:oil ratio	[69]
Sulfonated-carbonized de-oiled canola meal	65	MeOH:oil molar ratio=60	Canola oil containing high % FFAs	7.5 wt%	24	93.8%	1. Good reusability 2. High yield	1. Very high alcohol/ oil molar ratio 2. Slow reaction	[71]
Sulfonated-carbonized/activated Biochar	65	MeOH:oil molar ratio=15	Canola oil	5 wt%	3	18.9	1. Larger surface area 2. Larger pores 3. Active in transesterification	1. Poor reusability due to SO_3H leaching	[23]
Sulfonated-carbonized lignin	120	MeOH:oil molar ratio=12	Jatropha oil containing high % FFAs	5 wt%	5	96.3%	1. Moderate temperature 2. Moderate alcohol/oil ratio 3. Reusability		[72]

Table 4 (*continued*)

Catalyst	Reaction conditions					Conversion/ yield	Advantage	Disadvantage	Ref.
	Temperature (°C), others	Amount and type of alcohol	Vegetable oil/ triglyceride	Catalyst loading	Reaction time (h)				
$PhSO_3H$-OMCs	65	EtOH:oleic acid molar ratio = 10	Oleic acid	20 mg	1.25	77.7%	1. Better reusability than directly sulfonated-ACs 2. Ultra-high BET surface area 3. High and strong acid density	1. Not tested in transesterification	[62,85]
Sulfonated-carbonized corncobs	80	MeOH:oil molar ratio = 32	Model waste feedstock oil, 12 wt% FFAs	3 wt%	6	98%	1. High $-SO_3H$ density 2. Active for esterification/ transesterification 3. High FAME yield	1. Reusability due to $-SO_3H$ leaching 2. High MeOH:oil molar ratio	[76]
Sulfonated-carbonized glycerin	80	MeOH:oil molar ratio = 60	Triolein	10 wt%	12	25–26%	1. Very high acid density (about 5.3 mmol/g) higher than the sugar catalysts 2. Active in transesterification 3. Improved reusability, due to reduced SO_3H leaching	1. High methanol:oil molar ratio	[78]
Sulfonated lignin	70	MeOH:oil molar ratio = 9	Acidified soybean soapstock (56 wt% FFAs)	7 wt%	5	97% (FFA conversion)	1. Prepared in one-step 2. Reusability	1. Transesterification activity not reported	[79]
Base functionalized carbon catalysts									
Amine grafted-MWCNTs	60	MeOH:oil molar ratio = 12	Glyceryl tributyrate	Not specified	8	77%	1. Basic in nature (P^{ka} = 10.75) 2. Reusability	1. Not tested in transesterification of vegetable oils	[88]
Supported carbon catalyst									
Base supported carbon catalysts									
CaO supported on nanoporous carbon (NC-2)	60	MeOH:oil molar ratio = 6	Triacetin	2.0 wt% (with 12% CaO loading on NC-2 support)	4	≥ 99%	1. High activity 2. Mild reaction conditions 3. Reusability 4. High surface area 5. Reduced leaching, deactivation 6. Reduced sensitivity to water in comparison to CaO	1. Less active compared to unsupported CaO 2. Not tested in transesterification of vegetable oils	[89]
CaO supported on graphitic oxide (GO)	60	Soybean oil = 16.0 mL, methanol = 13.3 mL	Soybean oil	0.42 g	2	98.3	1. High activity 2. Mild reaction conditions 3. Reusability 4. High surface area 5. Reduced leaching, deactivation 5. Reduced sensitivity to water in comparison to CaO		[90]
CaO supported on activated carbon	120	MeOH:oil molar ratio = 40	Waste cooking oil	11 wt%	7	96%	1. Reduced leaching 2. Improved water a FFA tolerance 3. Reusability	1. Lower activity in comparison to CaO 2. Low surface area	[91]

KOH supported on palm shell activated carbon	64.1	MeOH:oil molar ratio = 24	Palm oil	30.3 wt%	1	97.72%	1. Mild reaction conditions	1. Low reusability, due to KOH leaching 2. High catalyst loading 3. High alcohol:oil ratio	[92]
Acid supported carbon catalysts									
12-Tungstophosphoric acid (TPA) impregnated on AC		MeOH:oil molar ratio = 6	Canola oil containing 10% FFA	3 wt%	6	65%	1. High surface area and pore volume	1. Slow reaction 2. Low activity	[94]
Enzyme supported carbon catalysts									
Lipase immobilized on AC	40, incubated with constant shaking at 300 rpm	MeOH:oil molar ratio = 6	Palm oil	50 mg	32–45	FAME yield ≥ 40%	1. High yield 2. Improved lipase stability	1. Slow reaction	[96,97]

optimized reaction conditions the physicochemical properties of biodiesel product were found to be with standard specifications of ASTM standard [93].

12-Tungstophosphoric acid (TPA) impregnated on active carbon was also reported to be active in simultaneous esterification and transesterification of waste canola oil. In their study 12-tungstophosphoric acid (TPA) impregnated on four different supports such as hydrous zirconia, silica, alumina and activated carbon. TPA supported AC exhibited a very high surface area of 1003 m^2/g and pore volume of 0.59 cm^3/g. TPA supported on alumina, silica and activated carbon exhibited almost similar ester yield of about 65 wt% for the transesterification of canola oil containing 10% FFA under identical reaction conditions while TPA supported on hydrous zirconia (TPA/HZ) was found to be the most active catalyst showing 77 wt% ester yield irrespective of TPA loading. The higher activity of zirconia supported TPA catalysts was attributed to the Lewis acidity arising due to the stronger interactions between TPA and –OH groups of zirconia. However, compared to strong heterogeneous alkali catalysts (CaO) these carbon-supported catalysts presented much lower activity [94].

Lipase (an enzyme catalyst usually used in biodiesel synthesis) [95] was also successfully immobilized onto activated carbon (carbon cloth, granular activated carbon). Naranjo et al. used *Candida antarctica* B lipase supported on granular activated carbon and activated carbon cloth as an enzyme catalyst in the synthesis of biodiesel from palm oil. Their study showed that lipase activation was reduced in the AC supported lipase catalyst. However, slight deactivation was still observed. The use of less polar alcohols like isopropanol, isobutanol, 1-butanol, 1-propanol, etc. during transesterification was found to have less of a negative effect on lipase stability in comparison to the traditionally used methanol. In the present study this behavior was mainly attributed to the unfavorable viscosity conditions, which affect the intimate mixing of substrates with lipase [96]. These results were consistent with the results obtained using methanol in the lipase-catalyzed alcoholysis of sunflower oil yielding only traces of methyl esters [95]. High FAME yields up to 100% (for ethanol) were recorded by stepwise addition of alcohol [96]. Similar results were also reported by Giraldo et al. by Lipase supported on mesoporous materials as catalyst. In the reactions carried out with methanol, ethanol, propanol, 2,2-dimethyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol, 100% yield was obtained with 3-methyl-1-butanol, since the immobilization lipase activation was reduced but not entirely absent. It was reported that the degree of deactivation of supported lipase catalyst was inversely proportional to the number of carbon atoms in the linear lower alcohols which determined the polarity of the alcohol. They observed that due to the decreasing of stability the immobilized lipase particles underwent a conspicuous change in appearance accompanied by swelling and caking. High yields of biodiesel could be achieved, but only with a stepwise addition of alcohol, as before. This work showed that alcohols with more than three carbon atoms were completely miscible with palm oil at a researched molar ratio. The experimental results indicated that one of the main causes of lipase deactivation was the immiscibility between triglycerides and short chain alcohols (i.e. methanol or ethanol). It is possible that short linear alcohols formed small droplets which attached to the resin particles and the alcohol were adsorbed to the immobilized enzyme resulting into the blocking of triglycerides finally causing the reaction to stop [97].

3. Discussion

Directly sulfonated-ACs are most studied of all the carbon based catalysts discussed here. The basic idea is to obtain a –SO_3H containing

solid material that can substitute homogeneous conc. H_2SO_4 usually used as a catalyst in esterification and transesterification reactions during biodiesel synthesis. According to the studies by different researchers, it has been well established that any carbon rich material such as sugars, glycerol, cellulose, Kraft lignin, vegetable or petroleum oil asphalt, nanotubes, active carbon, and biochar could be used as precursor [21,64,66,68,72,74,75,77]. Carbonization of these sources under inert atmosphere forms the graphite like material containing sufficient graphene frameworks required for surface sulfonation/functionalization. Studies also indicated that the catalytic activity is primarily determined by total acid density, $–SO_3H$ density, surface functional groups and pore structure. It is established that a high $–SO_3H$ density and pore volume favored high activity. These properties in turn are directly influenced by the carbonization temperature; all studies in the literature suggest that the use of moderate temperatures 400–600 °C generated catalysts with the highest activity due to relative ease of sulfonation and the presence of large quantities surface functional groups in the carbonized materials. The surface area of such materials was found to be usually very low (1 m^2/g or less) indicating that activity is independent of surface area. However, recent studies with similar catalysts obtained from activated biochar/AC showed that if surface area is high it may favor high activity. But the active $–SO_3H$ groups (usually located in the bulk) get exposed and consequently are easily leached resulting in the loss of activity upon reuse [23,74,75]. It has been suggested that the lost activity may be easily regained by sulfonating it again. Nevertheless, this is the cheapest way to prepare acid functionalized AC catalysts till date (Scheme 2). Use of glycerol, a byproduct of biodiesel synthesis, as starting material provides a more sustainable route of synthesis for such solid acid catalyst. By the in situ partial carbonization of waste glycerol under hydrothermal reaction conditions similar catalysts were also prepared but with higher activity (higher acid densities and larger surface area) and better stability. Such catalysts usually have high thermal stability (<260 °C) [77]. On the other hand, sulfonation by reductive alkylation/arylation of sulfonic acid containing aryl radical (Section 2.1.1.2) is more preferable due to higher yields, use of mild reaction conditions and no structural alteration/changes in the carbon framework following sulfonation which is crucial in order to preserve the high surface area and porosity of carbon material. Using this method sulfonated carbon catalysts with ultra high surface area ($\sim$1000 m^2/g), a bimodal pore size distribution and high strong acid density (1.86 mmol H^+/g) were produced [55,62,83]. Apart from these there are numerous other reports on the preparation of similar sulfonated carbons catalysts, by one step hydrothermal carbonisation/sulfonation [98], polymerization followed by sulfonation and carbonisation [99], by the thermal treatment of p-toluenesulfonic acid [100], etc., but they have been omitted in our discussion as the catalysts were not applied for biodiesel synthesis.

Only limited articles reporting the synthesis and use of base functionalized carbons are available. For e.g., various amine functionalized nanotubes, graphene showed high activity in transesterification and hydrolysis reactions, but studies are yet to be performed with long chain fatty acids and vegetable oils [86,87].

On the other hand, AC could also be used as a support material for preparing various supported AC catalysts. By simple incipient-wetness impregnation method many active catalysts like CaO, lipase, KOH, etc. were easily impregnated onto carbon surface [89–91]. The method is simple and cost effective for generating supported catalysts. Use of AC as support reduces cost and many structural drawbacks present in the active phase (metal oxides, metals, lipase, etc.). As for e.g., by immobilizing CaO particles on carbon support many of its disadvantages like low surface area, water sensitivity and leaching of active sites by polar species (e.g., glycerol, water) were overcome [90,91]. Similarly lipase deactivation was reduced by its immobilization onto carbon support. Overall, the activity of these carbon catalysts is determined by the % loading, nature (acid, base strength) and type of interaction between the carbon support and active phase [96–97]. A comparison of the specific features of the different carbon based catalysts employed in biodiesel synthesis has been summarized in Table 4.

4. Conclusion

The two key reactions in biodiesel production are the Esterification and Transesterification. These reactions are influenced mainly by the type of feedstock oil, reaction conditions, catalyst used and alcohol to oil molar ratio. Use of carbon-based (AC) catalysts in these reactions opens doors for cost minimization and environmentally benign biodiesel production by eliminating problems associated with the conventionally used reaction schemes (employing homogeneous catalysts commonly H_2SO_4, KOH or NaOH). As reported by different researches owing to its high thermal stability, unique surface and structural properties it can be utilized as a support for the variety of active catalysts (metal, metal oxide and so on). Moreover, due to structural resemblance of AC with graphite or graphene sheets, it is possible to attach different acidic or basic functional groups, creating a diverse class of new materials having unique structural features (of the carbon materials) and catalytic properties depending upon the nature of attached molecule/group (acidic or basic), with the possibility to be utilized as heterogeneous catalysts in different reactions including biodiesel synthesis.

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